

Photocurrents in nanotube junctions

D. A. Stewart* and François Léonard
Sandia National Laboratories, Livermore, CA 94551

Photocurrents in nanotube p - n junctions are calculated using a non-equilibrium Green function quantum transport formalism. The short-circuit photocurrent displays band-to-band transitions and photon-assisted tunneling, and has multiple sharp peaks in the infrared, visible and ultraviolet ranges. The operation of such devices in the nanoscale regime leads to unusual size effects, where the photocurrent scales linearly and oscillates with device length. The oscillations can be related to the density of states in the valence band, a factor that also determines the relative magnitude of the photoresponse for different bands.

Since their discovery[1], Carbon Nanotubes (NTs) have been the subject of intensive research due to their intriguing electronic and structural properties, and have demonstrated great promise for future nano-electronic devices[2]. However, their potential for opto-electronic applications has received much less attention, despite the ideal properties that NTs present. Indeed, a desirable property of opto-electronic materials is a direct band-gap, since it allows optical transitions to proceed without the intervention of phonons. NTs are unique in this aspect, since *all* the bands in *all* semiconducting NTs have a direct gap. Furthermore, the low dimensionality of NTs leads to a diverging density of states at the band edge and a high surface-to-volume ratio, reducing the sensitivity to temperature variations and allowing efficient use of the material. Finally, non-radiative transitions can significantly reduce the performance of conventional materials; NTs are believed to have low defect density, reducing non-radiative transitions.

These unique properties of NTs are only starting to be explored for opto-electronics. Recent experimental work[3] has shown that NT field-effect transistors can emit polarized light, while illumination of these and other NT devices generates significant photocurrent[4, 5]. Such observations have also been made in semiconductor nanowires[6, 7, 8]. Often, the observed opto-electronic effects are due to the presence of a p - n junction, with various physical realizations (electrostatically defined[3, 4], crossed-wire geometry[7], or modulated chemical doping[8].) Modulated chemical doping of individual semiconducting single-wall NTs to create “on-tube” p - n junctions has recently been reported in the literature[9]. These NT p - n junctions serve as excellent testbeds for understanding opto-electronics at reduced dimensionality.

Here we show that in simple NT p - n junctions, the photocurrent shows unusual features. Unlike traditional devices, the photoresponse in the NT junctions consists of multiple sharp peaks, spanning the infrared, visible and ultraviolet ranges. Furthermore, at nanoscale dimensions, the NT junctions show size effects, where the photocurrent scales and oscillates with device length.

We consider a NT p - n junction under illumination, as

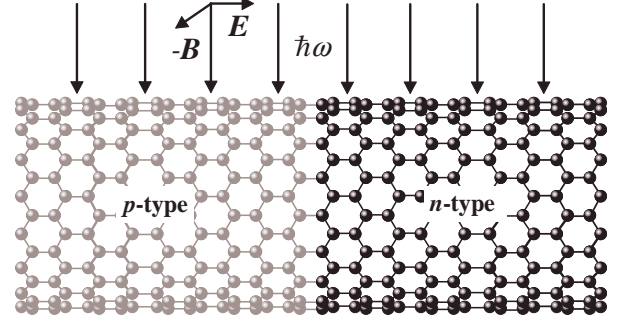


FIG. 1: Sketch of a portion of the scattering region for the (17,0) nanotube p - n junction. The scattering region is attached to two semi-infinite leads (not shown in figure). The incoming light of energy $\hbar\omega$ is polarized along the length of the nanotube, with electric field \mathbf{E} and magnetic field \mathbf{B} .

shown in Fig. 1. We use a (17,0) single-wall, semiconducting NT of radius 0.66 nm, and model the doping as in Ref. [10]. Our tight-binding Hamiltonian with one π orbital per carbon atom and nearest-neighbor matrix element of $\gamma = 2.5$ eV gives a direct band-gap for this NT of 0.55 eV. The incident light is assumed to be monochromatic, with polarization parallel to the NT axis.

To calculate the photocurrent, we use a non-equilibrium Green function formalism [11], in a real-space representation. The device consists of an illuminated scattering region connected to two dark semi-infinite leads, which are also doped (17,0) NTs. The structure of the (17,0) NT corresponds to parallel rings of 17 atoms, which are spaced by 0.07 nm and 0.14 nm. Each ring forms a layer in our system, with the rings in the scattering region labelled from 1 to N .

Since only layers 1 and N couple with the leads, the steady-state, time-averaged current can be written as

$$I = \frac{4e\gamma}{\pi\hbar} \int dE \operatorname{Re} [G_{N+1,N}^< + G_{1,0}^<]. \quad (1)$$

(This expression assumes that the hole current is equal and opposite to the electronic current and that the coupling of layers 1 and N to the leads is γ . The appropriateness of this equation for time-dependent Hamiltonians

is discussed in Ref. [12]) Here, $G_{N+1,N}^<$ and $G_{1,0}^<$ cross the scattering region boundary. To relate these terms to $G^<$ calculated entirely in the scattering region, we use the Dyson equations[13] $\gamma G_{1,0}^< = G_{1,1}^< \Sigma_{1,1}^{R0} + \Sigma_{1,1}^{<0} G_{1,1}^R$ and $\gamma G_{N+1,N}^< = G_{N,N}^< \Sigma_{N,N}^{R0} + \Sigma_{N,N}^{<0} G_{N,N}^R$. (We also note that in the presence of electron-photon interactions *and* the potential step in the p - n junction[12], $G_{N+1,N}^< \neq G_{1,0}^<$, an equality that would normally hold for a system without inelastic scattering.)

In the scattering region, $G^<$ is determined from the equations

$$G^< = G^R \Sigma^< G^{R\dagger} \quad (2)$$

and

$$G^R = [EI - H - \Sigma^R]^{-1}, \quad (3)$$

where H is the Hamiltonian for the NT p - n junction under illumination. The functions Σ^R and $\Sigma^<$ represent the interaction of the scattering region with the semi-infinite (17,0) NT leads and the incident light. In the presence of the electron-photon interaction, these functions depend on $G^<$, and the equations are coupled and non-linear. To simplify the calculation, we perform an expansion to first order in the light intensity: $G^< = G^{<0} + G^{<(ph)}$, $G^R = G^{R0} + G^{R(ph)}$, $\Sigma^< = \Sigma^{<0} + \Sigma^{<(ph)}$ and $\Sigma^R = \Sigma^{R0} + \Sigma^{R(ph)}$, where the order zero functions represent the dark p - n junction. In the absence of an applied bias, the only current in the device is the photocurrent

$$I^{(ph)} = \frac{4e\gamma}{\pi\hbar} \int dE \operatorname{Re} \left[G_{N+1,N}^{<(ph)} + G_{1,0}^{<(ph)} \right], \quad (4)$$

where

$$G^{<(ph)} = G^{R0} \Sigma^{<(ph)} G^{R0\dagger} + G^{R0} \Sigma^{R(ph)} G^{R0} \Sigma^{<0} G^{R0\dagger} + G^{R0} \Sigma^{<0} \left(G^{R0} \Sigma^{R(ph)} G^{R0} \right)^\dagger. \quad (5)$$

Here $G^{R0} = [EI - H_0 - \Sigma^{R0}]^{-1}$, with the Hamiltonian H_0 and the self-energy function Σ^{R0} describing the p - n junction without incident light, including the electrostatic potential. (The Hamiltonian matrix elements are $H_0^{2l,2l-1} = H_0^{2l-1,2l} = 2\gamma \cos(\frac{\pi J}{M})$, $H_0^{2l,2l+1} = H_0^{2l+1,2l} = \gamma$, and $H_0^{l,l} = -eV_l$, where V_l is the electrostatic potential on layer l). The self-energies Σ^{R0} due to the semi-infinite leads are calculated using a standard iterative approach[14], and $\Sigma^{<0} = -2f \operatorname{Im} \Sigma^{R0}$ where f is the Fermi function. The electrostatic potential and charge distribution are determined using a self-consistent procedure as in Ref. [10]. The last two terms in Eq. (5) are proportional to $f(E)$, while, as discussed below, the first term is proportional to $f(E - \hbar\omega)$. As long as the Fermi level is in the bandgap and not too close to the conduction band edge, the ratio $f(E)/f(E - \hbar\omega)$ is small, so we neglect the last two terms in Eq. (5). A benefit of this

approach is that a model for $\Sigma^{R(ph)}$ does not have to be formulated. (Including electron-hole recombination and other multi-photon processes requires going beyond the perturbation scheme introduced here, and is beyond the scope of this paper. At low light intensities, our calculations should provide a reasonable approximation.)

To derive the function $\Sigma^{<(ph)}$ due to the electron-photon interaction, we use the interaction Hamiltonian

$$H_{el-ph} = \frac{e}{m} \mathbf{A} \cdot \mathbf{p} \quad (6)$$

where \mathbf{A} is the time-dependent electromagnetic vector potential, \mathbf{p} is the electronic momentum operator and m is the electron mass. Following the procedure of Ref. [15], we obtain

$$\Sigma_{lm}^{<(ph)}(E) = \frac{2e^2 a^2 \gamma^2 F}{\hbar \omega c \varepsilon} \sum_{pq} P_{lp} P_{qm} G_{pq}^{<0}(E - \hbar\omega), \quad (7)$$

with

$$P_{lm} = \begin{cases} -1 & l - m = -1, l \text{ even} \\ +1 & l - m = 1, l \text{ odd} \\ -\cos\left(\frac{\pi J}{M}\right) & l - m = -1, l \text{ odd} \\ +\cos\left(\frac{\pi J}{M}\right) & l - m = 1, l \text{ even} \\ 0 & \text{otherwise} \end{cases} \quad (8)$$

In these equations, $a = 0.07$ nm is the smallest ring separation, $\hbar\omega$ is the photon energy, c is the speed of light and ε is the permittivity of free space. J is the circumferential angular momentum, labeling each of the $M = 17$ bands of the NT. Conservation of J is enforced, as required for light polarization parallel to the tube axis[16]. The photon flux F represents the strength of the incoming radiation, in units of photons per unit time per unit area. Since the photocurrents calculated in this work are proportional to F , we focus on the photoresponse I/eF . (This definition of the photoresponse might seem awkward at first, having units of area/photon. However, the unusual size effects in the nanotube devices are more transparent with this definition.) Because $G^{<0} = -2f \operatorname{Im} G^{R0}$, $\Sigma_{lm}^{<(ph)}(E)$ is proportional to $f(E - \hbar\omega)$.

Figure 2a shows the calculated self-consistent band diagram for the NT p - n junction for a doping of 5×10^{-4} electrons/C atom. The figure shows the conduction and valence band edges of the band with the smallest band gap, $J = 6$, shifted by the local electrostatic potential. The band bending is characterized by a step at the junction and flat bands away from the junction region[17].

The calculated photoresponse for this device at zero bias when 128 rings are illuminated is shown in Fig. 2b. The photoresponse due to bands $J = 6, 5, 7, 4, 3, 8$ (increasing band gap) is separately plotted in the figure (bands 11, 12, 10, 13, 14, 9 are equivalent). The general trend is for the photoresponse for the different bands J

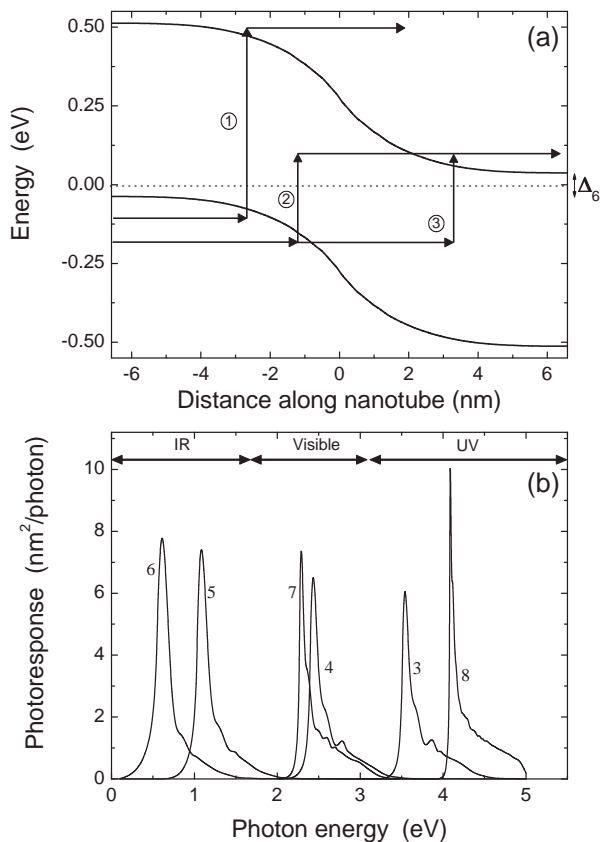


FIG. 2: Panel (a) shows the calculated self-consistent band diagram for the NT p-n junction. Solid lines are the valence and conduction band edges for the $J = 6$ band. Dotted line is the Fermi energy level. Path 1 represents a band-to-band transition while paths 2 and 3 represent photon-assisted tunneling. Panel (b) shows the calculated photoresponse for this device, plotted separately for each band J (labelled with the value of J in the figure).

to peak at higher photon energies as the band gap increases. Because the scattering cross-section decreases with $\hbar\omega$ [the $(\hbar\omega)^{-1}$ factor in Eq. (7)], one would expect the maximum photoresponse attained for each band to decrease with band gap. Surprisingly, the height of the peaks in Fig. 2b does not follow this behavior; in particular the response for band $J = 8$ is actually larger than the response for band $J = 6$. This is a result of the different bands having different effective masses. Indeed, the effective mass for $J = 8$ is about 36 times larger than for $J = 6$, leading to a much larger density of states near the edge of the valence band. (The role of the density of states will be discussed further below.)

Path 1 in Fig. 2a shows a band-to-band transition with the absorption of a photon of energy $\hbar\omega = 0.6$ eV. An electron coming from the p -type side of the device in the valence band absorbs a photon and is excited to the conduction band, where it then continues to the n -type

terminal. Such a transition is allowed when the photon energy exceeds the band gap E_g (0.55 eV for band 6). Band-to-band photocurrents in the NT device in the left lead due to electrons coming from the n -type terminal vanish unless the photon energy is larger than the band gap plus the potential step across the junction, $\hbar\omega \gtrsim 1$ eV in Fig. 2b. This asymmetry in the currents to the left and right terminals leads to the net photocurrents in Fig. 2b.

While these band-to-band transitions explain part of the photoresponse, a significant response exists at energies below the band gap. Such contributions can be attributed to photon-assisted tunneling. Paths 2 and 3 in Fig. 2a show two possible paths for photon-assisted tunneling. For a given band J , this process can only occur when $\hbar\omega > \Delta_J$, where Δ_J is the difference between the asymptotic conduction band edge on the p -type side and the asymptotic valence band edge on the n -type side (equal to 0.06 eV for the $J = 6$ band shown in Fig. 2a). The photon-assisted tunneling thus turns on at $\hbar\omega = \Delta_J$. As the photon energy increases above Δ_J , more states in the band gap become available for transport, and the photoresponse increases. For the bands with larger band gaps, the tail due to photon-assisted tunneling is less important relative to the band-to-band peak, since tunneling probabilities decrease with band gap.

The photoresponse of the different bands leads to multiple sharp peaks in three different regions of the electromagnetic spectrum: infrared, visible and ultra-violet. This unusual behavior arises because all the bands in the NT have a direct band-gap, which leads to a response over a wide energy spectrum. The separation of this wide response into peaks grouped in different regions of the electromagnetic spectrum is due to the particular electronic band structure of the NT, which has groups of bands separated by relatively large energies. The conduction band edges for $J = 6$ and $J = 5$ (infrared response) are separated from those of bands 4 and 7 (visible response) by about 0.6 eV, which are in turn separated by about 0.5 eV from the $J = 3$ and $J = 8$ conduction band edges (ultraviolet response). Since the photocurrent consists of an excitation from the valence band to the conduction band, the separation in Fig. 2b is twice these values.

In conventional bulk junctions, the photoresponse depends only on the dimensions of the device *perpendicular* to current flow. The nanotube device however shows a dependence with *length*, as shown in Fig. 3. Panel (a) in the figure shows the photoresponse of band $J = 6$ for different lengths of the illuminated region. As the illuminated region becomes longer, the peak in the photoresponse increases and also moves to lower energies. This behavior leads to linear scaling of the photoresponse with the length of the illuminated region, as the integrated photoresponse in the inset of Fig. 3a shows. The photoresponse for three different photon energies is shown in

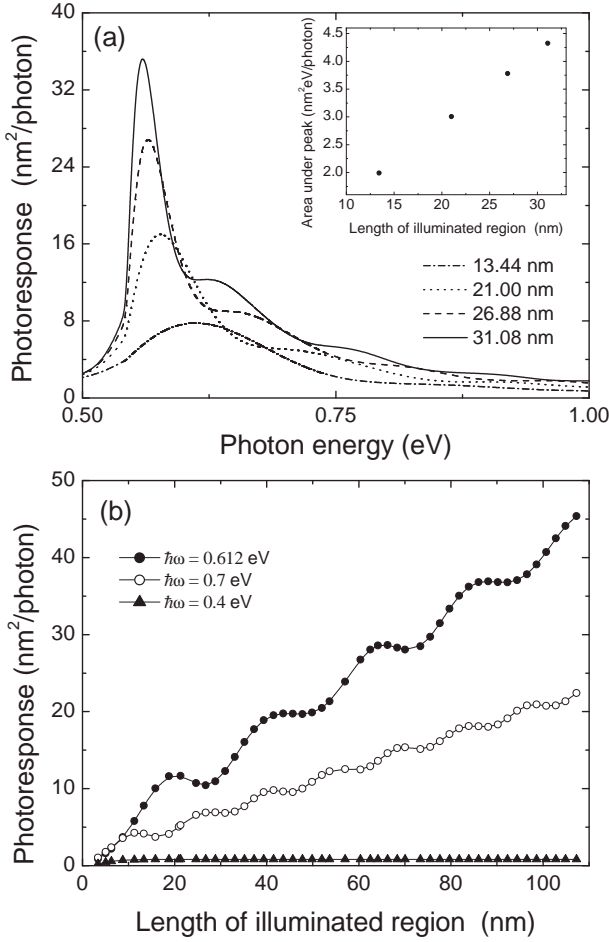


FIG. 3: (a) Dependence of the photoresponse for band $J = 6$ on the length of the illuminated region. The inset shows the integrated photoresponse, and its linear scaling with length. The response for different photon energies is shown in (b).

Fig. 3b. Clearly for $\hbar\omega = 0.4$ eV (photon-assisted tunneling) the photoresponse saturates with length, due to the fact that the wavefunctions in the band gap decay exponentially away from the junction. The response for $\hbar\omega = 0.612$ eV and $\hbar\omega = 0.7$ eV shows a completely different behavior, oscillating around a general linear increase.

These surprising results can be understood from a simplified description of the photocurrent in the nanotube. To this end, we note that the photocurrent density flowing to the right lead ($I_R^{(ph)} = \frac{2e}{\pi\hbar} \int i_R(E) dE$) can be expressed as

$$i_R(E) = -\Gamma_R \text{Im} \left(G^{R0} \Sigma^{<(ph)} G^{R0\dagger} \right)_{NN} \quad (9)$$

where $\Gamma_R = -2i \text{Im} \Sigma_{NN}^{R0}$. (Eq. (9) can be obtained from Eq. (1) by using Dyson's equation $\gamma G_{N+1,N}^{<} = G_{N,N}^{<} \Sigma_{N,N}^{R0} + \Sigma_{N,N}^{<0} G_{N,N}^R$, the relation $G_{i,j}^{<} = -G_{j,i}^{<*}$ and the condition that the net current must vanish for the

dark junction at zero bias.) At zero bias, $G^{<0}$ is purely imaginary, and therefore so is $\Sigma^{<(ph)}$. The above equation becomes

$$i_R(E) = -\Gamma_R \sum_{k,p} \text{Im} \Sigma_{kp}^{<(ph)} \{ \text{Re} G_{Nk}^{R0} \text{Re} G_{Np}^{R0} + \text{Im} G_{Nk}^{R0} \text{Im} G_{Np}^{R0} \}. \quad (10)$$

For a given outgoing electron energy E and photon energy $\hbar\omega$, we have found numerically that the argument of the summation is peaked around the diagonal $k = p$. Taking only these contributions, we obtain

$$i_R(E) \sim -\Gamma_R \sum_k \text{Im} \Sigma_{kk}^{<(ph)} |G_{Nk}^{R0}|^2. \quad (11)$$

The photocurrent in the NT can thus be understood in terms of the excitation of electrons in each layer k along the NT (the $\text{Im} \Sigma_{kk}^{<(ph)}$ term in the above equation), and the subsequent transmission to the lead by G_{Nk}^{R0} .

To explain the linear scaling, we note that for $\hbar\omega > E_g$ and $E > E_c^{-\infty}$ where $E_c^{-\infty}$ is the asymptotic value of the conduction band edge on the p -type side of the device, there is a section of the NT where band-to-band transitions are allowed, and the sum in the last equation is dominated by this section of the NT. As the length of the illumination region is increased, a longer section of the NT is available for band-to-band transitions, leading to the linear scaling of the current with length.

While this explains the linear scaling, there remains the questions of the oscillations in the photoresponse and the dependence of the photoresponse on the effective mass. To address this, we note that $\text{Im} \Sigma_{kk}^{<(ph)}(E)$ contains terms like $\text{Im} G_{kk}^{<0}(E - \hbar\omega)$, which are related to the density of states at layer k , D_k , through $\text{Im} G_{kk}^{<0}(E - \hbar\omega) = \pi f(E - \hbar\omega) D_k(E - \hbar\omega)$, with $f(E)$ the Fermi function. Therefore, the photocurrent is sensitive to the density of states at energy $E - \hbar\omega$. This explains the origin of the dependence on the effective mass, and the relative height of the peaks in Fig. 2.

Figure 4 shows the valence band density of states for $J = 6$, calculated at layer 11 for systems with illuminated lengths of 24.78, 26.88, and 28.98 nm. (This is the density of states near the edge of the illuminated region, which is moving further away from the junction as the length increases). The density of states contains many peaks, and as the system size changes, the peaks move in energy. Because the propagator $|G_{Nk}^{R0}|^2$ is sharply peaked at energy $E_c^{-\infty}$, the photoresponse is particularly sensitive to the density of states at $E_c^{-\infty} - \hbar\omega$. At that energy, the density of states oscillates as a function of the distance from the p - n junction, as illustrated in the inset of Fig. 4. This leads to the oscillations in the photoresponse as a function of illumination length shown in Fig. 3b. The oscillation wavelength of the density of states increases for energies closer to the band edge, causing the different oscillation wavelengths for $\hbar\omega = 0.612$ eV and $\hbar\omega = 0.7$ eV in Fig. 3b.

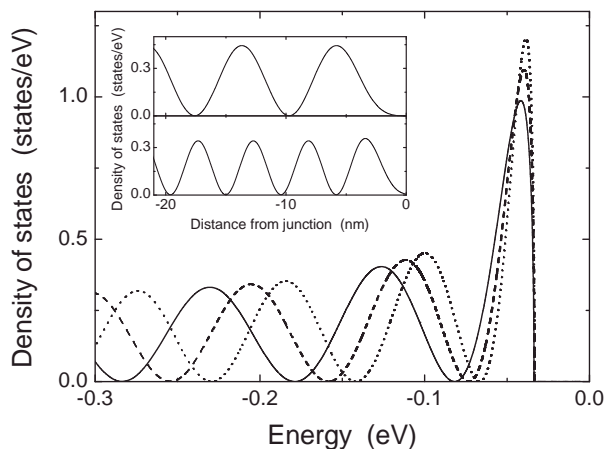


FIG. 4: Density of states at layer 11 as a function of energy. Solid, dashed, and dotted lines are for illumination lengths of 24.78, 26.88, 28.98 nm respectively. The top (bottom) inset shows the density of states on the even rings at energy -0.1 eV (-0.2 eV).

Although the device presented here is fairly simple, it already shows the richness of new phenomena that arises in nanoscale opto-electronics. One may envision several uses for this or related devices (photodetection, power generation, optical communication, etc.), but the important point is that the behavior is much different from traditional devices and must be taken into account in future device development.

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* dstewar@sandia.gov

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